

recovered propane is recycled to the reactor (Stream 6) for cooling. The remainder (Stream 7) can be returned to a refinery for use as feedstock or fuel gas.⁷⁹

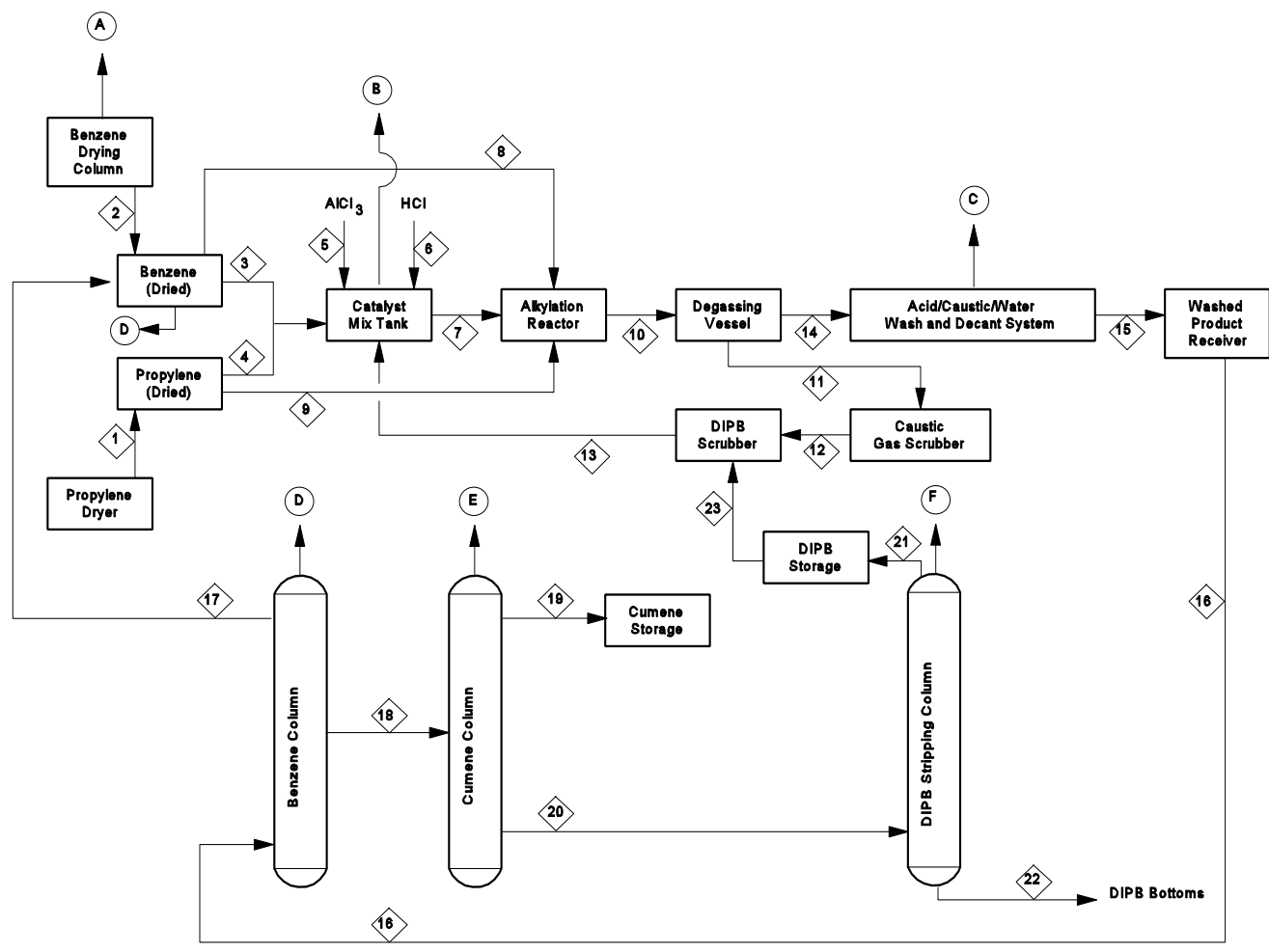
Unpurified product from the depropanizer (Stream 8) is sent to the benzene distillation column, where unreacted benzene is recovered overhead (Stream 9), sent through a condenser, and recycled to the feed drum (Stream 10). From the bottom of the benzene column (Stream 11), the crude product is sent to the cumene distillation column, where the high-purity cumene is separated from heavy aromatics and then condensed (Stream 12) and stored (Stream 13). The bottoms (compounds of relatively lower volatility) from cumene distillation (Stream 14) contain primarily diisopropylbenzene and are sent to a refinery or used as fuel gas.⁷⁹

The cumene distillation column is normally operated slightly above atmospheric pressure and is padded with methane (or nitrogen) to protect the cumene from contact with the air. As the pressure fluctuates, a pressure-control valve relieves excess pressure on this system by bleeding off a mixture of methane (or nitrogen) and cumene vapor (Vent A).⁷⁹

Aluminum Chloride Catalyst Process

The production of cumene using an aluminum chloride catalyst is similar to that using a solid phosphoric acid catalyst. The aluminum chloride method requires additional equipment to dry recycled streams and to neutralize reaction products. Figure 5-8 shows a typical process diagram for cumene manufacture using aluminum chloride as the alkylation catalyst. Aluminum chloride is a much more active and much less selective alkylation catalyst than solid phosphoric acid.⁷⁹

The aluminum chloride used as a catalyst in this process is received and handled as a dry powder. To prevent undesirable side reactions, the propylene used with this catalyst system must be of chemical grade (95 percent pure) and must contain no more than minute amounts of other olefins such as ethylene and butylene. This propylene feedstock must also be



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Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 5-8. Process for the Manufacture of Cumene Using Aluminum Chloride Catalyst

Source: Reference 80.

dried and treated (Stream 1) to remove any residual organic sulfur compounds. The benzene used in this process must be azeotropically dried (Stream 2) to remove dissolved water. The azeotrope drying distillation generates a vent gas (Vent A) that is rich in benzene.⁷⁹

Benzene and propylene (Streams 3 and 4) are fed to a catalyst mix tank, where the aluminum chloride powder (Stream 5) is added. This mixture is treated with HCl gas (Stream 6) to activate the catalyst. The catalyst preparation operation generates a vent gas consisting of inert gases and HCl gas saturated with vapors of benzene and diisopropylbenzene. A scrubber is typically used to absorb the HCl gas and the residual vapors are then vented (Vent B). The resulting catalyst suspension (Stream 7) and additional dried benzene (Stream 8) are fed to the alkylation reactor as liquids, and additional dried propylene (Stream 9) is introduced into the bottom of the reactor. The feed ratio to the alkylation reactor is maintained at or above four moles of benzene per mole of propylene to inhibit side reactions.⁷⁹

The crude reaction mixture from the alkylation reactor (Stream 10) is sent to a degassing vessel, where hydrocarbons such as propane are released from solution (Stream 11). This vapor stream is scrubbed with a weak caustic solution and then fed (Stream 12) to the diisopropylbenzene (DIPB) scrubber, where the hydrocarbon vapor is recontacted with DIPB to extract residual unreacted propylene. The stream containing the propylene (Stream 13) is sent to the catalyst mix tank.⁷⁹

The degassed product (Stream 14) is sent to the acid wash tank, where it is contacted with a weak acid solution that breaks down the catalyst complex and dissolves the aluminum chloride in the water layer. The crude product from the acid wash tank is sent to a decanter tank, where the water is removed. The product is then sent to a caustic wash tank, where any residual acid in the product is extracted and neutralized. The product is decanted again to remove water and then enters a water wash tank, where it is mixed with fresh process water. This process water extracts and removes any residual salt or other water soluble material from the product. The product from the water wash tank is sent to a third decanter tank, where the crude product and water settle and separate.⁷⁹

The entire wash-decanter system is tied together by one common vent-pad line that furnishes nitrogen for blanketing this series of tanks. A pressure control valve on the end of the vent-pad manifold periodically releases vent gas (Vent C) as levels rise and fall in the various tanks of the wash-decanter system. The vent gas is saturated with water vapor and hydrocarbon vapor (principally benzene) as contained VOC.⁷⁹

The washed and decanted product (Stream 15) is stored in a washed-product receiver tank. The crude product from the washed-product tank (Stream 16) is sent to a recovery column, where the excess benzene is stripped out. The recovered benzene (Stream 17) is returned to the benzene feed tank. The vent line associated with the benzene recovery column and with the benzene receiver tank releases some vent gas (Vent D). This vapor is principally inert gas saturated with benzene vapor as contained VOC.⁷⁹

The crude cumene (Stream 18) is sent to the cumene distillation column for distillation of the cumene product. The cumene product (Stream 19) is then stored for sale or in-plant use. The cumene distillation column and the associated cumene receiver tank are operated above atmospheric pressure and are blanketed with nitrogen (or methane) to protect the cumene from reacting with oxygen in the air and forming cumene hydroperoxide. The vent line associated with the cumene distillation column and with the cumene receiver tank releases some vent gas (Vent E). This vent gas is nitrogen (or methane) saturated with cumene vapor as the contained VOC.⁷⁹

The bottoms from the cumene distillation column contain a small amount of cumene, along with mixed isomers of diisopropylbenzene and a small amount of higher-boiling alkylbenzenes and miscellaneous tars. The bottoms stream (Stream 20) is sent to a DIPB stripping column, where DIPB is recovered and then stored (Stream 21). This stripping column is normally operated under vacuum because of the high-boiling points of the DIPB isomers. The vacuum system on the stripping column draws a vent stream from the column condenser, and this vent stream is air (or inert gas) saturated with cumene and DIPB vapors as

the contained VOC. Depending on the design and operation of the vacuum system for the column, part or all of the vent gas could be discharged to the atmosphere (Vent F).⁷⁹

The bottoms from the DIPB stripper (Stream 22) are stored in a receiver tank and then sent to waste disposal for use as a fuel. The recycle DIPB (Stream 23) is sent to the DIPB scrubber, where it is used to absorb residual propylene from the propane waste gas stream. This recycle DIPB eventually returns to the alkylation reactor, where it is transalkylated with excess benzene to generate additional cumene.⁷⁹

5.3.2 Benzene Emissions From Cumene Production

Information related to benzene emissions from process vents, equipment leaks, storage vessels, wastewater collection and treatment systems, and product loading and transport operations associated with cumene production is presented below. Where a literature review has revealed no source-specific emission factors for uncontrolled or controlled benzene emissions from these emission points, the reader is referred to Section 5.10 of this chapter, which provides a general discussion of methods for estimating uncontrolled and controlled benzene emissions from these emission points.

Benzene Emissions from the Solid Phosphoric Acid Catalyst Process

In the solid phosphoric acid process, potential process vent emissions of benzene may be associated with the cumene column vent (Vent A in Figure 5-7). Using methane to pressurize the system, the process operates at a pressure slightly higher than atmospheric pressure to make sure that no air contacts the product.⁸⁰ The methane is eventually vented to the atmosphere, carrying with it other hydrocarbon vapors.⁸⁰

No specific emission factors were found for benzene emissions from the cumene column. One factor for total VOC emissions indicated that 0.015 lb (0.03 kg) of total VOC are emitted per ton (Mg) of cumene produced, and that benzene constituted a “trace amount”

of the hydrocarbons in the stream.⁸⁰ One cumene producer has indicated that it uses a closed system (all process vents are served by a plant flare system). Thus, it is possible that there are no process vent emissions occurring directly from the production of cumene, although there may be emissions from the flares.⁷⁹

Benzene Emissions from the Aluminum Chloride Catalyst Process

Process vent emissions of benzene from the production of cumene using an aluminum chloride catalyst are associated with the benzene drying column (Vent A in Figure 5-8), the scrubber or the catalyst mix tank (Vent B), the wash-decanter system (Vent C), the benzene recovery column (Vent D), the cumene distillation system (Vent E), and the DIPB stripping system (Vent F).⁸⁰ No specific emission factors were located for benzene emissions from these sources. However, as presented in Table 5-5, one reference provided total VOC emission factors and estimates of benzene percent composition of the emissions.^{3,80} The percent (weight) of benzene may be used along with a cumene production volume to calculate an estimate of benzene emissions from these sources. The control technique most applicable to these sources is flaring, with an estimated efficiency of at least 98 percent (see Section 4.5.1 of this chapter for further discussion of this control device).

5.4 PHENOL PRODUCTION

Most U.S. phenol (97 percent) is produced by the peroxidation of cumene, a process in which cumene hydroperoxide (CHP) is cleaved to yield acetone and phenol, as well as recoverable by-products α -methylstyrene (AMS) and acetophenone. Phenol is also produced by toluene oxidation and distillation from petroleum operations.^{81,82} Table 5-6 shows the locations, capabilities, and production methods of the phenol producers in the United States.^{11,81,83} Because benzene may be present in the feedstock, it may be emitted during production of phenol.

TABLE 5-5. SUMMARY OF EMISSION FACTORS FOR CUMENE PRODUCTION
AT ONE FACILITY USING THE ALUMINUM CHLORIDE CATALYST

SCC and Description	Emission Source	Control Device	Emission Factor in lb/ton (kg/Mg) ^{a,b}	Factor Rating
3-01-156-02 Cumene Manufacturing - Benzene Drying Column	Process Vent	Uncontrolled	4.00×10^{-2} (2.00×10^{-2})	U
		Flare	2.00×10^{-3} (1.00×10^{-3})	U
3-01-156-03 Cumene Manufacturing - Catalyst Mix Tank Scrubber Vent	Process Vent	Uncontrolled	3.18×10^{-1} (1.59×10^{-1})	U
		Flare	1.59×10^{-2} (7.95×10^{-3})	U
3-01-156-04 Cumene Manufacturing - Wash-Decant System Vent	Process Vent	Uncontrolled	1.57×10^{-2} (7.85×10^{-3})	U
		Flare	7.84×10^{-4} (3.92×10^{-4})	U
3-01-156-05 Cumene Manufacturing - Benzene Recovery Column	Process Vent	Uncontrolled	3.40×10^{-2} (1.70×10^{-2})	U
		Flare	1.70×10^{-3} (8.50×10^{-4})	U

Source: References 3 and 80.

^a Factors are expressed as lb (kg) benzene emitted per ton (Mg) cumene produced.

^b Derived by multiplying the total VOC emission factor by percent of benzene in the stream.

TABLE 5-6. U.S PRODUCERS OF PHENOL

Facility	Location	Annual Capacity million lb (million kg)	Process and Raw Material
Allied-Signal, Inc. Engineering Materials Sector	Philadelphia, PA	810 (367)	Cumene peroxidation
Aristech Chemical Corporation	Haverhill, OH	630 (286)	Cumene peroxidation
BTL Specialty Resins Corporation	Blue Island, IL	90 (41)	Cumene peroxidation
Dakota Gasification Company	Beulah, ND	50 (23)	Petroleum and coal tar
Dow Chemical U.S.A.	Oyster Creek, TX	550 (249)	Cumene peroxidation
General Electric Company GE Plastics	Mount Vernon, IN	640 (290)	Cumene peroxidation
Georgia Gulf Corporation	Pasadena, TX	160 (73)	Cumene peroxidation
	Plaquemine, LA	440 (200)	Cumene peroxidation
Kalama Chemical, Inc.	Kalama, WA	70 (32)	Toluene oxidation
Merichem Company	Houston, TX	35 (16)	Petroleum and coal tar
PMC, Inc.	Santa Fe Springs, CA	8 (3.6)	Petroleum and coal tar
Shell Chemical Company Shell Chemical Company, Division	Deer Park, TX	600 (272)	Cumene peroxidation
Stimson Lumber Company Northwest Petrochemical Corporation, Division	Anacortes, WA	<5 (<2.3)	Petroleum

(continued)

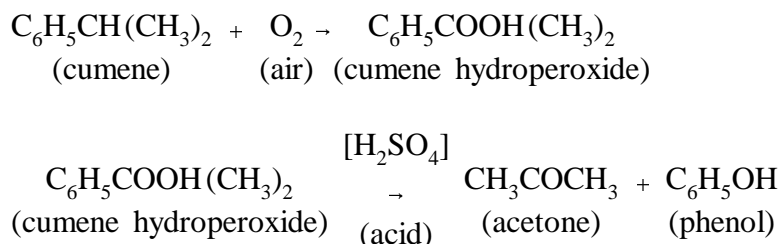
TABLE 5-6. CONTINUED

Facility	Location	Annual Capacity million lb (million kg)	Process and Raw Material
Texaco, Inc. Texaco Chemical Company, Subsidiary	El Dorado, KS	95 (43)	Cumene peroxidation
TOTAL		<3,398 (<1,541)	

Source: References 11, 81, and 83.

Note: This list is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current lists and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel. These data on producers and locations were current as of November 1993.

In the process involving peroxidation of cumene, acetone and phenol are produced by the peroxidation of cumene followed by cleavage of the resulting CHP. The two basic reactions for this process are as follows:⁸⁰



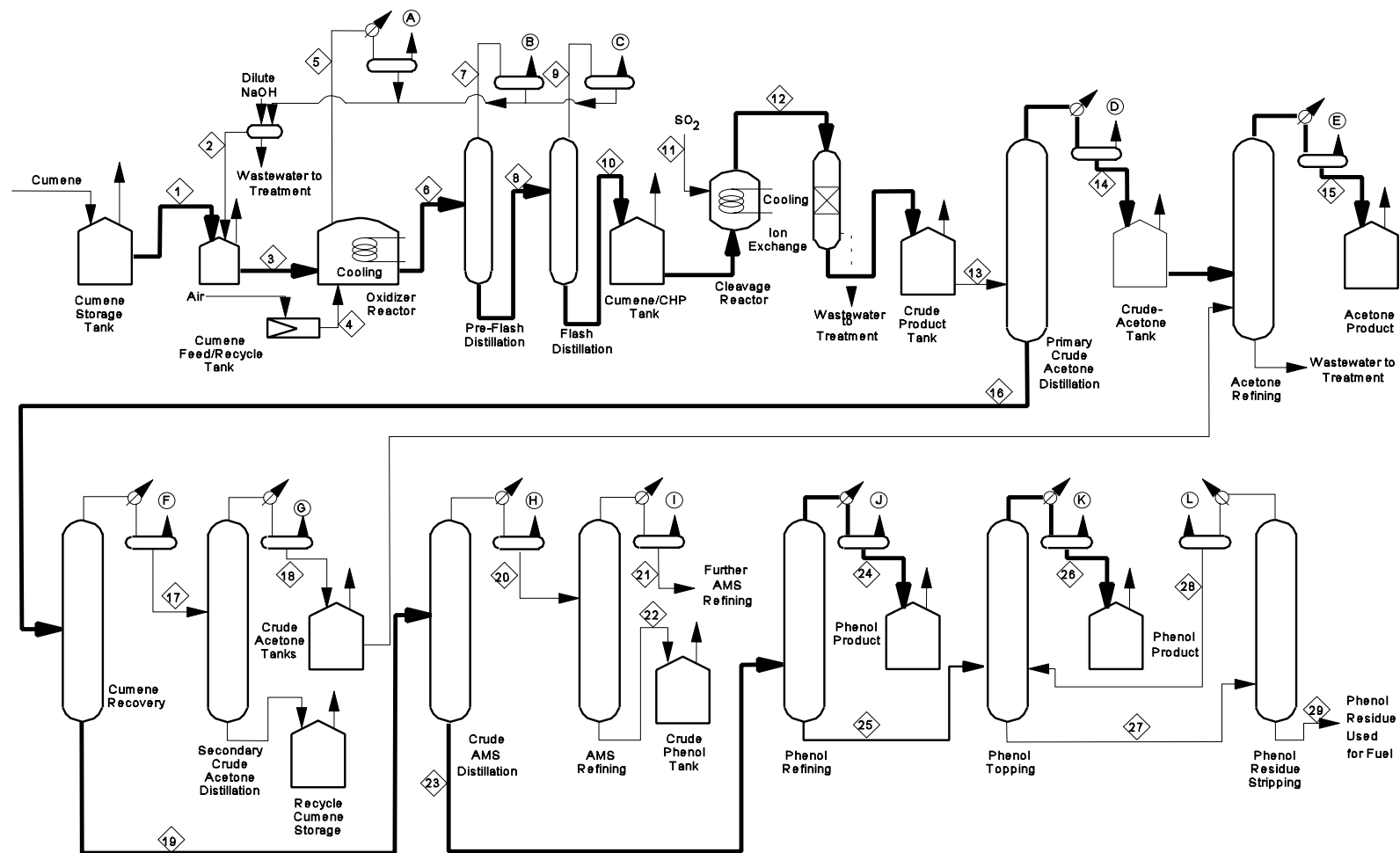
5.4.1 Phenol Production Techniques

There are two technologies for producing phenol by the peroxidation of cumene--one licensed by Allied Chemical and the other licensed by Hercules. The major differences between the Allied and Hercules processes involve the operating conditions of the peroxidation reaction and the method of neutralization of the acid in the cleavage product. These differences affect plant design primarily in the peroxidation and cleavage-product neutralization steps, in the location of process emission points, and in the potential quantity of process emissions. These two process types are discussed below.⁸⁰

In addition to the two cumene peroxidation processes, phenol is produced by the oxidation of toluene. This process is described below; however, the description is brief because of limited available information on the process.

Allied Process

Figure 5-9 shows a typical flow diagram for the manufacture of phenol by the Allied process.⁷⁹ Cumene (Stream 1), manufactured on site or shipped to the site, and recycle cumene (Stream 2) are combined (Stream 3) and fed with air (Stream 4) to the multiple-reactor system, where cumene is oxidized to form CHP. Substantial quantities of cumene (Stream 5) are carried out of the reactors with the spent air to a refrigerated vent system, where part of the



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions. Lines in bold indicate the flow of the product stream.

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Figure 5-9. Flow Diagram for Phenol Production from Cumene Using the Allied Process

Source: Reference 79.

cumene is recovered and recycled.⁸⁰ Uncondensed vapors, including organic compounds, are vented (Vent A).

The reaction product (Stream 6), containing primarily cumene and CHP, is vacuum flashed first in the pre-flash distillation column and then (Stream 8) in the flash distillation column to remove most of the cumene, which is recycled (Streams 7 and 9). Uncondensed vapors, including organic compounds, are vented (Vents B and C). The concentrated CHP (Stream 10) flows through the CHP concentrate tank to the cleavage reactor, where the CHP is cleaved to acetone and phenol by the addition of SO₂ (Stream 11). The cleavage product (Stream 12) is neutralized in ion-exchange columns and fed through the crude-product surge tank (Stream 13) to a multi-column distillation system.^{80,84,85}

In the primary crude acetone distillation column, acetone and lower-boiling impurities such as acetaldehyde and formaldehyde are distilled overhead. This product (Stream 14) is condensed and flows through the crude acetone surge tank to the acetone refining column, where the acetone is distilled overhead. Acetone product is condensed (Stream 15) and sent to storage. Uncondensed vapors, including organic compounds, are vented from the condensers after both the primary crude acetone and acetone refining columns (Vents D and E).^{80,84}

The compounds of relatively lower volatility (bottoms) from the primary crude acetone column (Stream 16) are distilled in the cumene recovery column to remove residual cumene. The overheads from the cumene recovery column are sent through a condenser (Stream 17) and into a secondary crude acetone distillation column to further remove acetone from the residual cumene. The residual cumene (i.e., the bottoms from the secondary crude acetone column) is stored for recycling.⁸⁰ The uncondensed vapors from the condensers, following both the cumene recovery column and secondary crude acetone column are vented (Vents F and G). The condensed overheads from the secondary crude acetone column (Stream 18) are fed through a crude acetone surge tank back to the acetone refining column.

Some facilities using this process may not incorporate the secondary crude acetone distillation column, which is utilized both to further recover acetone product and to reduce organic emissions from the storage tanks containing the recycle cumene. Some processes store the condensed product from the overhead of the cumene recovery column as the recycle cumene (Stream 17).

The bottoms from the cumene recovery column (Stream 19) contain primarily phenol, AMS, acetophenone, and other organics with higher boiling points than phenol. This stream is fed to the crude AMS distillation column. The crude AMS distillation column overhead stream (Stream 20) is condensed and sent to the AMS refining column. Uncondensed vapors from the condenser after the crude AMS distillation column are vented (Vent H). The stream entering the AMS refining column undergoes distillation to refine out AMS. The refined overhead stream is condensed (Stream 21) and sent to additional columns (not shown) for further refining.

The uncondensed vapors from the condenser following the AMS refining column are vented (Vent I). The bottoms from the AMS refining column (Stream 22) are stored in a crude phenol tank. The phenol in this storage tank is either sold as crude product or is fed to the phenol refining column for further refining. Crude phenol from the bottom of the crude AMS column (Stream 23) flows to the phenol refining column, where phenol is distilled overhead, condensed, (Stream 24), and fed to phenol product storage tanks. The uncondensed vapors from the condenser following the phenol refining column are vented (Vent J).^{80,84,85}

The bottoms from the phenol refining column (Stream 25) are further processed to recover phenol. The bottoms are sent to a phenol topping column, from which the overhead stream is condensed (Stream 26) and fed to phenol product storage. Uncondensed vapors from the condenser after the phenol topping column are vented (Vent K). The bottoms from the phenol topping column (Stream 27) are fed to a phenol residue stripping column, which removes phenol residue in the bottoms (Stream 29). The phenol residue may be used as fuel

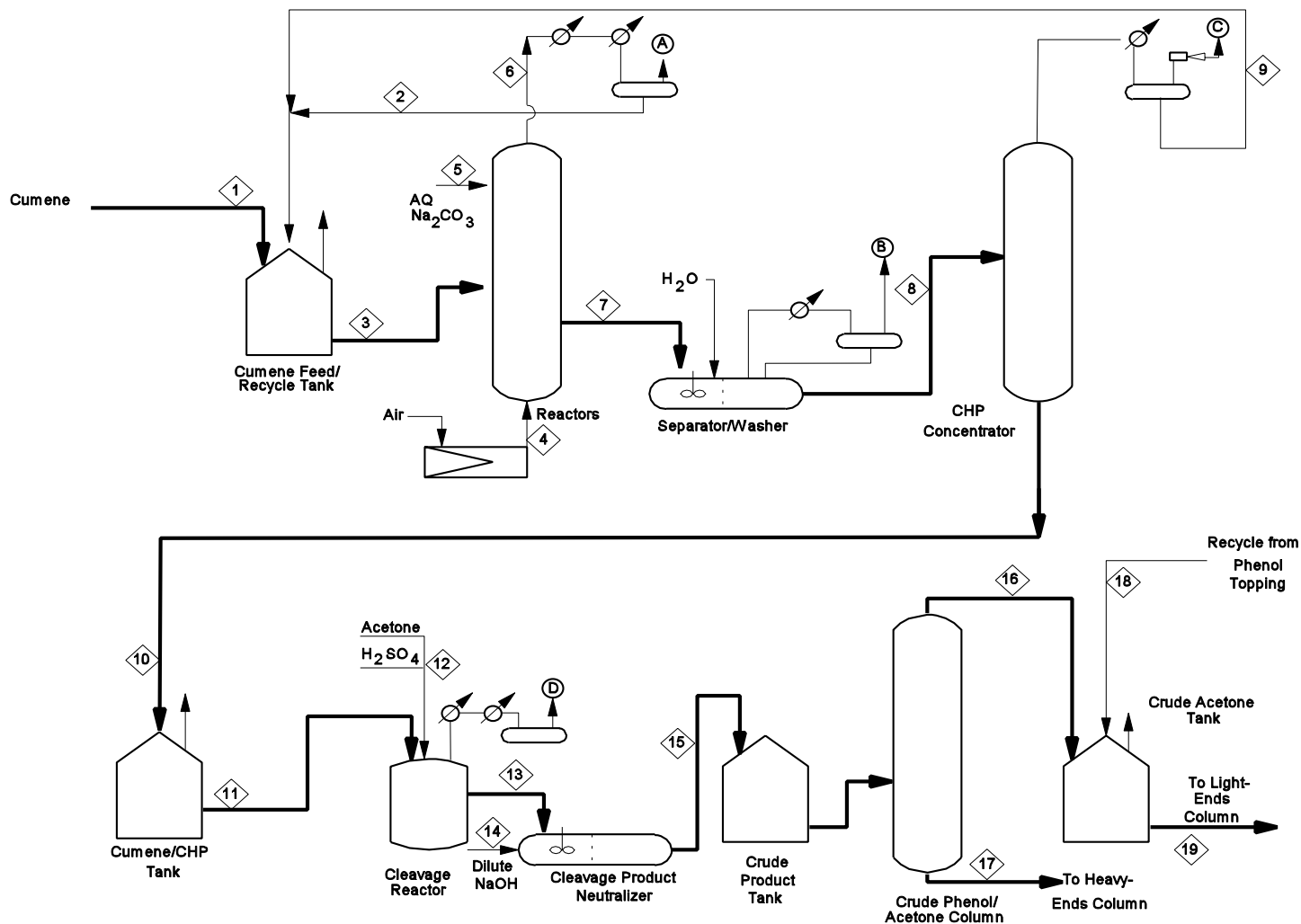
for on-site industrial boilers. The overheads from the phenol residue stripping column are condensed (Stream 28) and fed back to the phenol topping column to further recover phenol product. The uncondensed vapors from the condenser following the phenol residue stripping column are vented (Vent L).^{84,85}

The phenolic wastewater generated by the Allied process (e.g., generated by recovery devices, such as condensers and scrubbers) is fed through distillation columns to further recover acetone and phenol products. This batch distillation cycle, which is not a continuous process, is not shown in Figure 5-9. Phenolic wastewater is fed through a dephenolizer (i.e., a steam stripping process) and one or two batch distillation columns. The recovered product is crude phenol or acetol phenol.⁸⁴⁻⁸⁶

Hercules Process

Figure 5-10 shows a typical flow diagram for the manufacture of acetone and phenol by the Hercules process.⁷⁹ Cumene from storage (Stream 1) and recycle cumene (Streams 2 and 9) are combined (Stream 3) and then fed with air (Stream 4) to the multiple-reactor system. Additionally, an aqueous sodium carbonate solution (Stream 5) is fed to the reactor system to promote the peroxidation reaction. In the reactor system, cumene is peroxidized to cumene hydroperoxide. Unreacted cumene is carried out of the reactors with the spent air (Stream 6) to a refrigerated vent system, where part of the cumene is recovered and recycled (Stream 2). Uncondensed vapors are vented (Vent A).⁸⁰

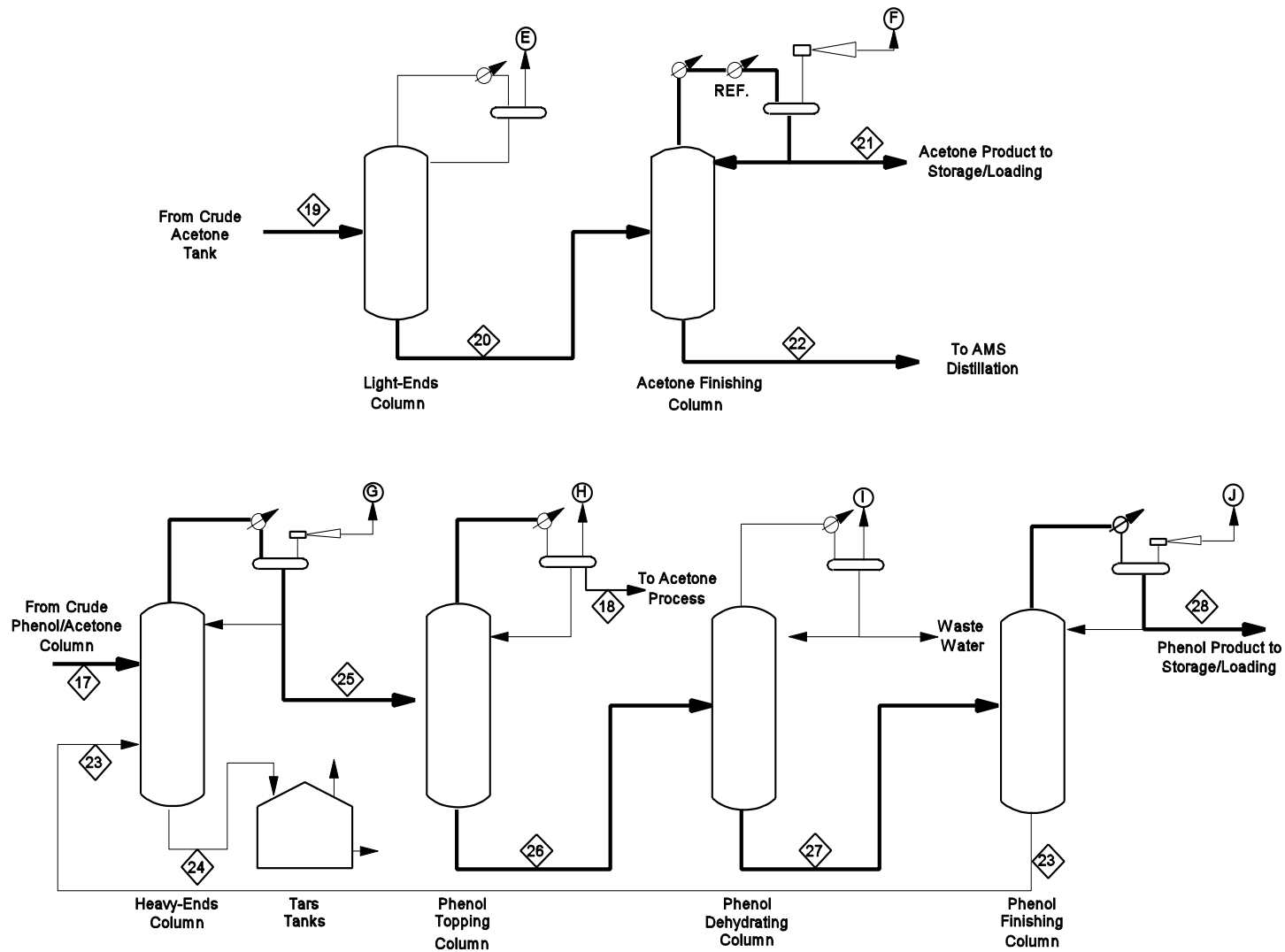
The oxidation reaction product (Stream 7) flows into a separator to remove spent carbonate solution and then is washed with water to remove remaining carbonate and other soluble components. The air stream removed is sent to a condenser from which uncondensed vapors are vented (Vent B). The washed product (Stream 8) is fed to a distillation column operated under vacuum, where the cumene hydroperoxide is separated from the cumene. The overheads from the CHP concentrator are condensed and the recovered



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions. Lines in bold indicate the flow of the product stream.

Figure 5-10. Flow Diagram for Phenol Production Using the Hercules Process

Source: Reference 79.



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions. Lines in bold indicate the flow of the product stream.

Figure 5-10. (Continued)